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Experimental studies on grain growth in metals

By H. U. Åström

With 12 figures in the text

Introduction

Interest in a better understanding of the interface-boundary phenomena has focussed attention on the grain boundaries and their energy relations. The experimental data published on the boundaries and their movements are, however, few and incomplete. The interfacial grain-boundary energies reported in the literature are all indirect, in the sense that they have been obtained by comparing the energy of a grain boundary with that of an external surface, the surface energy of which is determined, e.g. from the dihedral angles formed between the solid and a liquid of known surface tension. A more direct way to determine the grain-boundary energies, however, is to measure them calorimetrically. From the microscopic determination of the corresponding decrease of the grain-boundary area, the average specific boundary energy can be calculated. The purpose of the present paper is to give the results of calorimetric and microscopic studies on the grain-growth process in some metals of high purity. A preliminary report of measurements on the grain growth in zinc has been published elsewhere [1].

Calorimetric arrangements

The energy released when a metal with an average grain diameter of 10^{-2} mm undergoes normal grain growth, i.e. a uniform increase of the size of the grains, can be expected to be of the order 0.1 cal/mole. This is about 100 times smaller than the heat stored during cold-work, which is given off prior to or during recrystallization. The measurement of this small energy therefore demands a calorimetric apparatus working with very high accuracy. The precision vapour thermostats used earlier for the determination of small energies [2] are not convenient for this type of measurement as they do not at higher temperatures possess the extremely good stability necessary, owing to small irregularities in the vaporization of the boiling liquids. A thermostat working according to a different principle had therefore to be tried. The apparatus chosen was an electrically heated and regulated thermostat, the construction of which has been described earlier by Kelen [3]. The working principle of this thermostat is as follows. A controller periodically connects and disconnects part of the heating power, thereby causing small fluctuations of temperature of about some hundredths of a degree in a thick-walled aluminium tube, externally thermally insulated. The temperature-sensitive part of the controller is a resistance thermometer with a very small heat capacity placed in this tube. The controller keeps the mean temperature of the tube constant within certain limits of error by changing the ratio between on and off in each cycle. The temperature fluctuations of the tube propagate radially inwards over another concentric aluminium tube to an aluminium block with a large heat capacity at the centre of the thermostat. Due to construction of the thermostat the temperature fluctuations are strongly damped on their way from the heating elements to the axis of the thermostat. After a great deal of trimming work it was possible to have the apparatus operate with good temperature stability in the range 100° to 400°C, the variations being less than 0.0001°C per hour.

The specimen was located in an axial hole in the central block of the thermostat and a series of about 30 thermocouples connected via a commutator to a sensitive galvanometer, were arranged between the specimen and the wall of the thermostat in such a way that the deflection of the galvanometer was proportional to the rise in temperature of the specimen caused by the heat liberated during the growth process. The thermocouples consist of Au + 3 at% Ni and Au. The measuring cell was built in such a way that the thermal transition resistance between the sample and the surrounding junctions was small. One source of error influencing sensitive calorimetric measurements is disturbing electromotive forces in the leads from the thermopile to the commutator shifting the current to the galvanometer. These effects were, however, reduced by the use of wires of pure gold. The temperature of the room, where the thermostat was placed, must further be kept very constant.

The specimens

The calorimetric investigation was made with specimens in the form of a number of small granules of the metals with a diameter of a few millimeters and with a total mass of about one mole. The initial grain size of the specimens was in most cases about 0.1 mm. At first the calorimetric measurements were made in an atmosphere of argon, the granules being contained in a thin-walled aluminium tube fitting into the measuring cell. However, it was very difficult to avoid a slight oxidation effect due to a remainder of oxygen absorbed on the surfaces of the specimen. In some cases, this oxidation effect made it difficult to observe the small release of heat due to grain growth. In order to eliminate this disturbance, the granules were therefore placed in thin-walled argon-filled pyrex containers, which were evacuated and sealed.

The measurements

When beginning a calorimetric measurement the specimen was placed in a small oven, the temperature of which was held somewhat higher than that of the thermostat in order to have the specimen rapidly heated to the measuring temperature. The temperature of the specimen was controlled by means of a Pt-PtRh thermocouple located at the centre of the specimen. The moment the specimen had the same temperature as the thermostat it was introduced into the measuring device and the readings could start after the few minutes necessary to obtain thermal equilibrium. The measurements gave the rate of change of energy as a function of time. In order to obtain absolute values the apparatus was calibrated with a known amount of Peltier heat evolved at the junction of the thermocouple of the specimen. Fig. 1 shows the results of a measurement on silver at 285.0°C. The calorimetric run always

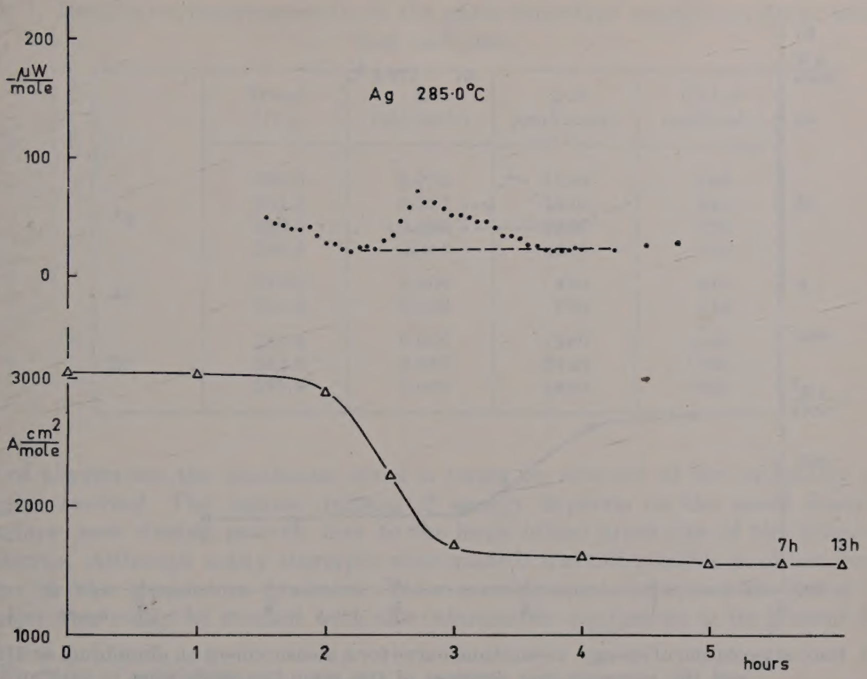


Fig. 1. Rate of evolution of energy- versus time-curve for a measurement on silver at 285.0°C and the corresponding decrease of the grain-boundary area.

began with a rapidly decreasing evolution of heat probably due to the annealing of small residual strains in the specimens. After this effect a small peak was obtained in the curve indicating a minute release of energy.

As a complement to the calorimetric measurements in each case the change of the grain structure was studied microscopically as a function of the annealing time at the same temperatures and using the same materials as in the calorimetric investigations. The preparation of the samples was made by polishing the metals electrolytically, using metallographic standard methods [4]. The grain-boundary area of the samples was estimated from the average number of intercepts with the grain boundaries per unit length of random lines in sections of the samples [5]. The decrease in boundary area corresponding to the calorimetric measurement mentioned is shown in the lower part of Fig. 1. The curve is of a sigmoidal form. During the first stage of anealing, the grain-boundary area decreased only very slowly. The length of this period becomes shorter as the annealing temperature is raised. The region to which most of the grain-boundary changes are concentrated coincides with the occurrence of the peak in the calorimetric curves. The assumption therefore suggests itself that this peak must depend on the release of energy during grain growth.

Results

(*a*) *Grain-boundary energies*

Five metals have been used in the present investigation, viz. zinc (99.94%), copper (99.999%), gold (99.9%), silver (99.9%), and aluminum (99.992%). Only in

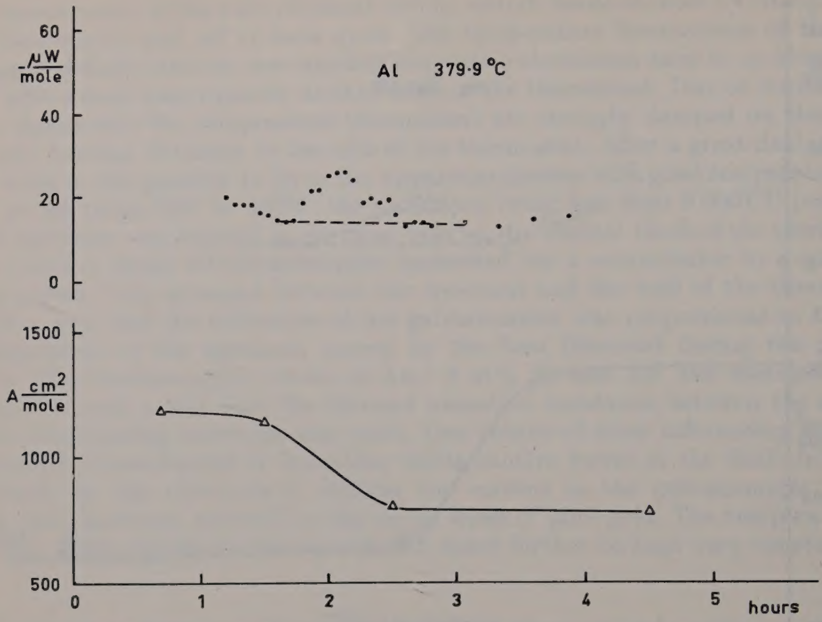


Fig. 2. Rate of evolution of energy- versus time-curve for a measurement on aluminium at 379.9°C and the corresponding decrease of the grain-boundary area.

three cases, zinc, silver and aluminium, however, grain growth of measurable speed was obtained inside the working range of the thermostat.

From microscopic studies of the decrease of the grain-boundary area it was found that the position of the peak in the calorimetric curves coincided with the region of rapid grain growth, where 80% or more of the changes in the boundary area were obtained. Outside this region the small evolution of energy from grain growth was disturbed by other processes which made the beginning and the end of this effect uncertain. On the other hand the energy release on account of the decrease of the boundary area must according to the microscopic results be so small in these regions that it is uncertain whether the sensitivity of the calorimetric apparatus is high enough to measure any effect here from the grain growth. For the estimation of the grain-boundary energy we have taken the integrated area of the peak curve although the beginning and the end of this curve are somewhat diffuse. This may of course introduce a certain error in the calculations. The corresponding change in the boundary area is determined from the size of the area at the ends of the peak.

Two of the measurements on silver and aluminium have been plotted in Figs. 1 and 2. A typical measuring curve for zinc was shown in the earlier paper [1]. The results of the calorimetric and the microscopic measurements are collected in Table 1. Here U is the grain-growth energy and ΔA the change in interfacial area. The specific grain-boundary energies are found in the last column. These values must be considered as average values for the large-angle boundaries of the metals. Due to many sources of error influencing the results of these measurements, the inaccuracy of the energies obtained is probably as high as about 20% for zinc and silver. In the

Table 1. Results on measurements on the grain-boundary energies in silver, aluminium and zinc.

	Temp. (°C)	U (cal/mole)	ΔA (cm^2/mole)	$U/\Delta A$ (erg/cm^2)
Ag	285.0	0.023	1200	800
	285.3	0.027	1340	845
	286.0	0.039	2255	720
	289.1	0.044	2325	790
Al	379.0	0.006	410	610
	382.5	0.006	390	640
Zn	281.4	0.052	1360	1580
	282.8	0.088	2140	1720
	283.6	0.068	1490	1920

case of aluminium the maximum error is larger on account of the extremely small energies evolved. The minute release of energy depends on the small changes of boundary area during growth due to the large initial grain size of the aluminium specimens. Although many attempts were made it was not possible to obtain smaller grains in the aluminium granules. These measurements represent the lowest limit of what can really be studied with the calorimetric equipment in its present form.

(*b*) *Energies of activation*

The dependence on temperature of the grain growth obtained from the calorimetric measurements could not be used for the calculation of the energy of activation for the process in the present cases as the initial conditions, viz. the grain size, varied a great deal from specimen to specimen. Estimation has therefore been based on the temperature dependence of the microscopically determined rate of change of the boundary area in comparable specimens. In Figs. 3–7 the microscopic curves of the change of boundary area at different temperatures are shown. Each point there is an average value of intercept measurements on some ten granules. For each metal the energy of activation for grain growth has been calculated at a given grain size. This grain size (the dotted line in the figures) was chosen as a weighted mean to the maximum rate of decrease of the area at the measuring temperatures of the metal, the velocities being determined directly from the difference between the experimental points. The velocities thus obtained are given in Table 2, and have been plotted in a logarithmic scale versus the reciprocal absolute temperatures in Figs. 8–12. The energies of activation obtained from the slope of these lines are given in Table 2 within an accuracy of about 15%.

Theoretical estimate of grain-boundary energies

The question of whether the present boundary energies in Table 1 are consistent with theoretical expectations cannot be answered properly as the large-angle boundaries are not yet amenable to exact quantitative treatment. One possible way is to treat the grain boundary as a homogeneously disturbed layer between the bonding grains, with a structure comparable to that of liquid metal. From different investigations it may be assumed that the breadth of the liquid zone is very restricted. Assum-

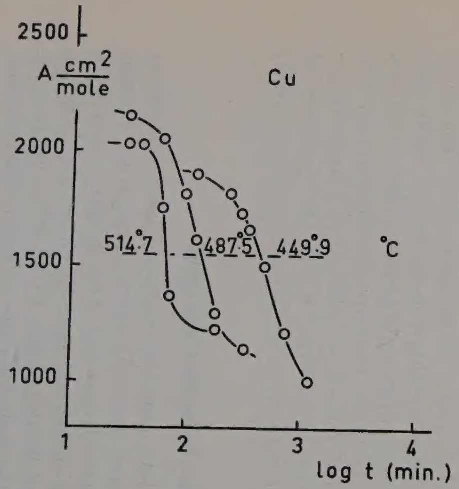


Fig. 3.

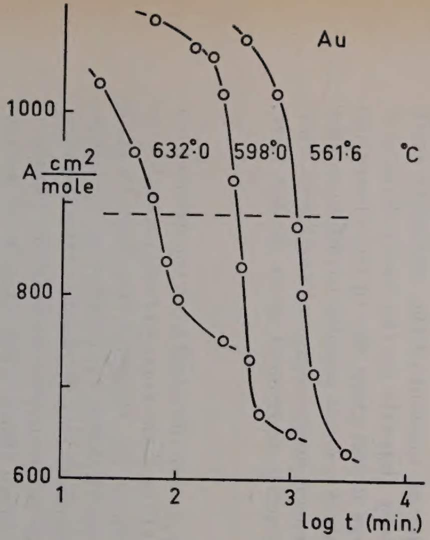


Fig. 4.

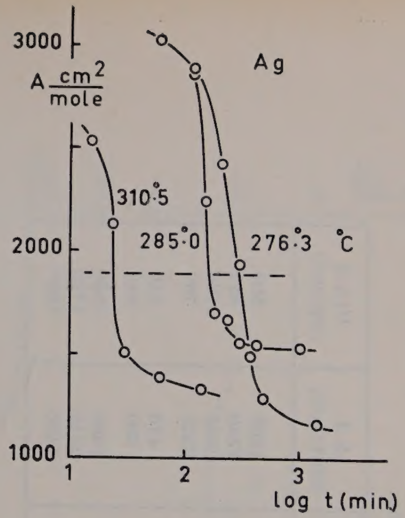
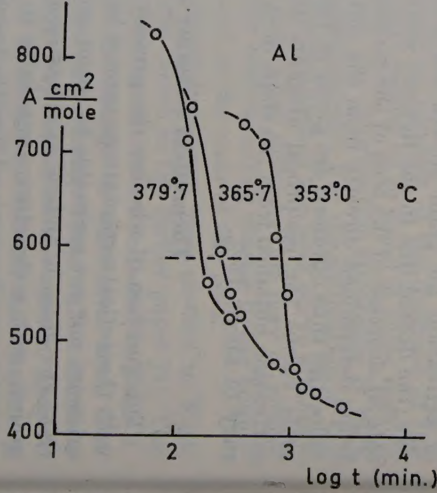
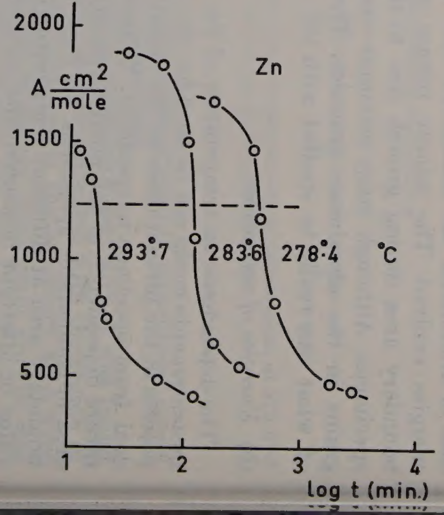


Fig. 5.





Figs. 3–7. Decrease of grain-boundary area per mole of specimen with increasing anealing time at different temperatures. The dotted line indicates the grain-boundary area at which the rate of changes of grain-boundary area was calculated for the determination of the energy of activation.

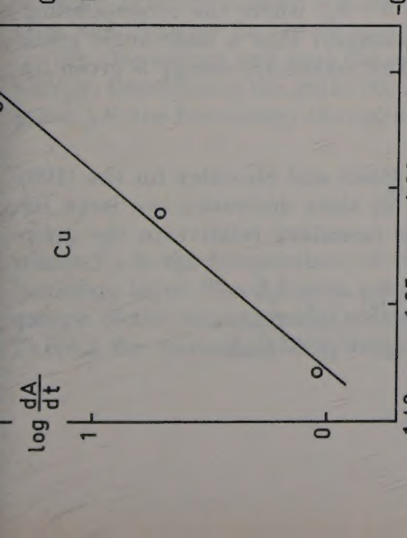


Fig. 8.

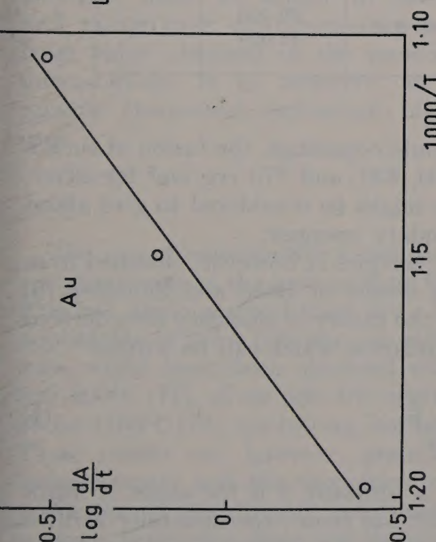


Fig. 9.

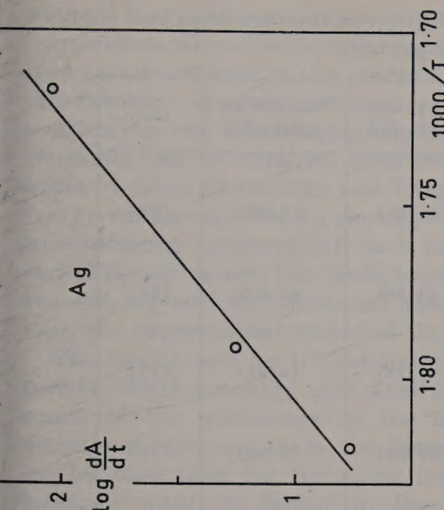


Fig. 10.

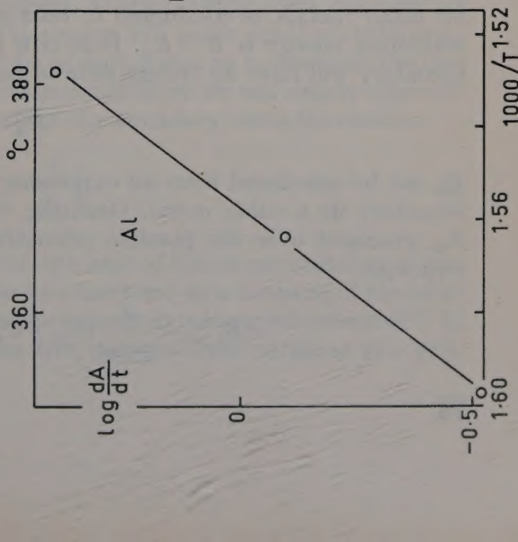


Fig. 11.

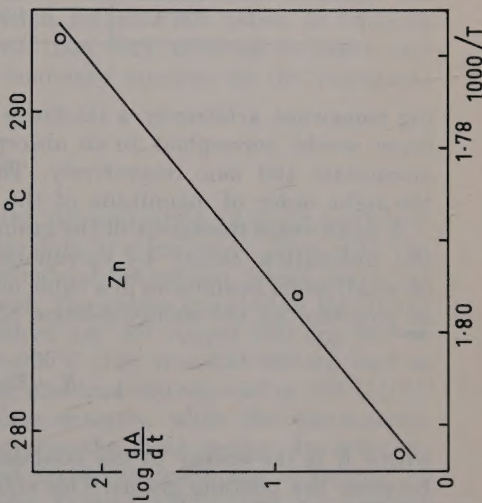


Fig. 12.

Figs. 8–12. Rate of change of boundary area in cm² per mole and minute versus the reciprocal of the absolute temperatures of the measurements.

Table 2. Rate of changes of boundary area at different temperatures and energies of activation for grain growth.

	Temp. (°C)	dA/dt (cm²/mole min)	$Q_{\text{gr. growth}}$ (cal/mole)	$Q_{\text{latt. self diff.}}$ (cal/mole)	Ref.
Cu	514.7	25.7	55 000	47 000	[19]
	487.5	5.2			
	449.9	1.1			
Au	632.0	3.3	49 000	45 000	[20]
	598.0	1.6			
	561.6	0.4			
Ag	310.5	110	57 000	44 000	[19]
	285.2	18.0			
	276.3	5.7			
Al	379.7	2.5	62 000	33 000	[19]
	365.7	0.8			
	353.0	0.3			
Zn	293.7	170	150 000	20 400 31 000	[19]
	283.6	7.3			
	278.4	1.9			

ing somewhat arbitrarily a thickness of two atomic c-spacings, the fusion of such a layer would correspond to an absorption of 900, 820, and 770 erg/cm² for silver, aluminium and zinc respectively. These values might be considered to give about the right order of magnitude of the grain-boundary energies.

A more exact treatment of the grain-boundary energies is, however, obtained from the dislocation theory by extrapolation of the results of Read and Shockley [6] on small-angle boundaries in a cubic metal. From the theory of elasticity they derived an equation for the energy relation of these boundaries, which can be written

$$E = E_0\,\theta\left(1 - \ln\frac{\theta}{\theta_m}\right), \tag{1}$$

where E is the energy of the boundary and E_0 a constant. θ is the angle of misfit between the bonding grains. This equation, which has been experimentally verified for many metals, is considered to hold good up to $\theta = \theta_m$, where the corresponding maximum energy is $E = E_m$. It is now generally assumed that a large-angle grain boundary will have an energy near to maximum. The maximum energy is given by

$$E_m = E_0\,\theta_m. \tag{2}$$

E_0 can be calculated from an expression given by Read and Shockley for the (100) boundary in a cubic metal. Omitting the details in their derivation we have for E_0, averaged over the possible orientations of the boundary relative to the grain structure,

$$\langle E_0\rangle_{\text{av}} = \frac{d}{\sqrt{2}\,\pi^2}\,[C_{11} + C_{12}]\sqrt{\frac{C_{44}\,[C_{11} - C_{12}]}{C_{11}\,[C_{11} + C_{12} + 2\,C_{44}]}}, \tag{3}$$

where d is the lattice constant and the elastic constants C_{11}, C_{12} and C_{44} refer to the temperature where the boundaries come to equilibrium. For silver the exact dependence on temperature of the elastic constants has not yet been determined, but from the values at absolute zero and room-temperature [7, 8] the values for the actual temperature can be extrapolated. For aluminium more accurate values of the elastic constants can be obtained from Sutton's measurements [9]. As to the maximum angle of misfit Greenough and King's [10] measurements of the relative boundary energy versus angle for Ag gave $\theta_m = 25°$ which angle is also accepted for Al, where no corresponding measurements have been reported up to the present time. Using these experimental values the grain-boundary energies obtained from eqs. (2) and (3) are 420 erg/cm^2 for silver and 400 erg/cm^2 for aluminium. These results are lower than the experimental values of the present investigation.

The model used for the estimation of the large-angle boundary energies in cubic metals would probably give misleading results for the hexagonal metals. On account of the anisotropy of the hexagonal metals it can be supposed that the density of dislocations in the large-angle boundaries will be considerably higher in this case than for the cubic materials. In addition the self-energy of the dislocations must be higher in the hexagonal case. Hence one could expect to find rather high grain-boundary energies in the hexagonal metals, wherefore the large value obtained in the present investigation for zinc not seems to be quite unreasonable. It is, however, at the present time very difficult to make any reliable theoretical estimation of the grain-boundary energies in the hexagonal case.

Discussion

The use of calorimetric measurements for the determination of grain-boundary energies seems at the present time to be possible only in a few cases. Even with the dihedral angle method there are a lot of experimental limitations, which make the application of it for this purpose rather restricted. The values reported in the literature, which have been obtained with this method are: for copper 550 erg/cm^2 at 800–900°C [11], silver 350–450 erg/cm^2 at 800–900°C [10], iron 850–950 erg/cm^2 at about 1100°C [12], tin 100 erg/cm^2 at 220°C [13], and lead 200 erg/cm^2 at 320°C [13]. These results are, however, grain-boundary free energies, while the calorimetric measurements and the theoretical calculations give the total energy. In order to make the values directly comparable we must try to estimate the difference in entropy between a grain and its boundary region. At the melting point it is obvious that the changes in the entropy term and in energy will make equal contributions to the free energy and that the entropy will be of such a sign as to decrease the free energy. Considering the grain boundary as a thin liquid layer we can simply approximate ΔF, the free energy change at the formation of a boundary, from the relation

$$\Delta F = \Delta L \left(1 - \frac{T}{T_m}\right), \tag{4}$$

where T_m is the temperature of fusion and ΔL the heat of fusion per unit area of the boundary layer. The ΔL term may in our case be considered as a measure of the total energy of the boundary and we therefore use the present experimental values of U in Table 1 for estimating ΔF with eq. (4). The free energies thus obtained are: 420, 190 and 340 erg/cm^2 for silver, aluminium and zinc respectively at the temperatures given in the table. There are values from both methods only for Ag. The agreement seems to be good. It must, however, be observed that the temperatures of measurement of the energies differ widely, and such a coincidence should therefore not be given too great consideration. It is, on the other hand, not possible to use the relation in eq. (4) for calculating the free energy at temperatures differing too much from those at which U has been measured.

The period of relatively slow decrease in the grain-boundary area observed at the beginning of the grain-growth process seems at first sight unaccountable as one could expect to get the maximum rate of decrease here. In contrast to most investigations, reported in the literature, we have not started with a cold-worked material but with a material as strain-free as possible. Furthermore the initial grain size was in our case fairly large. It is therefore probable that the grain-boundary movement should be strongly influenced by the interaction between the boundaries and the impurities in the metal. It has recently been pointed out [14] that moving dislocation walls, such as grain boundaries, may loose their solute atmospheres gradually during motion, at velocities up to a critical maximum, above which the atmospheres are entirely left behind. This interaction effect might well explain the slow boundary movement at the beginning of annealing. On the other hand on account of the large initial grain size we reach the upper limit of possible enlargement of the grains after a rather short period of growth.

It can be expected that the interaction between the impurities and the grain boundaries will be dependent on the temperature. It is therefore doubtful whether it is possible to derive heats of activation of general validity from the dependence on temperature of such quantity as, for instance, the rate of decrease of the grain-boundary area. It was furthermore observed by Beck [15] that the rate of grain growth varied with the grain size (at least in the case of aluminium). In order to have well defined energies of activation one must therefore use a rather restricted range of temperature for their determination and use velocities referred to the same grain size. In the present investigation we have tried to fulfill these requirements. Velocities have thus been determined at the same boundary area and the total range of temperature for the measurements has varied from 20 to 70°. Strictly speaking, the energies obtained are, however, nevertheless only valid at the temperatures of determination, and for the purities of the metals used.

Energies of activation for grain-growth in pure metals have earlier been reported for aluminium and silver. For the first metal Beck [15] gave a value of 71000–85000 cal/mole at 350 to 650°C. From the study of secondary recrystallization in silver, Alexander *et al.* [16] found an energy for the boundary movement of 28000 cal/mole at 430 to 530°C. Assuming the dislocation model for the large-angle boundaries, heats of activation for grain-growth of about the same magnitude as for the lattice self-diffusion may be expected. The present results on copper, gold and silver are within the limit of accuracy nearly equal to the values of self-diffusion collected in Table 2. The low value of Alexander [16] has been ascribed to the grain-boundary self-diffusion observed in silver [17]. Since our measurements were also undertaken in the actual temperature range of this diffusion effect and the purity of the metal used in the two cases seems to be about the same, the discrepancy in the energies of activation is rather astonishing. One possible reason for the differing results may be the fact that in [16] only one grain of favourable orientation was studied, while we used an average over many grains. In contrast to copper, gold and silver the energies of activation for aluminium and zinc are much greater than the corresponding energies for lattice self-diffusion. The high value of 62000 cal/mole in aluminium compared to 33000 cal/mole for self-diffusion may be an effect of the impurities in the grain-boundaries but the difference seems too high to be wholly due to the foreign atoms. The activation energy for recrystallization in aluminium of the same purity as in the present case is 58000 cal/mole [2]. This similarity can, however, be expected as it is probably a difference in quantity rather than in quality between the boundary movements of recrystallization and grain-growth. The high energy in the case of zinc may on the other hand depend on the anisotropy of the hexagonal metals. It was pointed out earlier in the discussion of the grain-boundary energy of zinc that the density of dislocations is probably higher in the hexagonal metals than in the cubic ones. It has also been observed [18] that the anisotropy of the thermal expansion of zinc leads to the formation of glide-steps in the grain boundaries by which the movement of the boundaries may be more complicated.

SUMMARY

A combination of calorimetric and microscopic methods has made it possible to determine the average specific energy of the large-angle boundaries in some pure metals. The values obtained are for Ag 790 erg/cm^2, Al 630 erg/cm^2, and Zn 1740 erg/cm^2 within an accuracy of some twenty per cent. These measurements give, however, the total energies while the results obtained earlier with the dihedral angle method are free energies. After subtracting a reasonable entropy therm the results of the two methods seem to be quite comparable in magnitude for silver. The extremely high energy of zinc is thought to be due to the anisotropy of the hexagonal metals which may influence the structure of the large-angle boundaries.

The energy of activation for grain-growth has been calculated from the microscopically determined rate of change of the boundary area for a fixed grain size at different temperatures. The following energies were obtained: Cu 55000, Au 49000, Ag 57000, Al 62000, and Zn 150000 cal/mole. It is concluded that these values are strictly valid only at the temperatures of the determination and for the purity of the metals used on account of a probable temperature and concentration dependence of the interaction between the impurities and the grain boundaries.

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Note added in proof. — The theoretical estimate of the grain-boundary energies for silver and aluminium showed that the calculated values were only half as large as the experimental ones. The size of this discrepancy depends, however, on the model of the boundary on which the calculations are based. Hence eq. (3) refers to a case where the grains have a common (001) axis with two sets of dislocations in the boundary with their slip vectors directed in [110] and [$1\bar{1}0$]. This arrangement of dislocations is energetically very favourable. Assuming a somewhat more complex structure of the boundary with four sets of dislocations all of which are half edge or half screw and with the slip vectors in [101] and [011] alternating with [10$\bar{1}$] and [01$\bar{1}$] the grain-boundary energies become higher. According to an expression derived by Read and Shockley [6] for this case the energies obtained are about 620 erg/cm^2 for silver and 470 erg/cm^2 for aluminium compared to 790 and 630 erg/cm^2 respectively from the calorimetric measurements. There may be other simple models giving still higher boundary energies. It is, however, not possible to decide which of these models corresponds best to the structure of the average large-angle boundary. Another point which makes the comparison of calculated and experimental values so difficult is the unknown influence of the impurities on the grain-boundary energies. In conclusion it can therefore be stated that it is not possible at present to decide whether the main reason for the discrepancy is to be found in the approximations and averages used in the calculations or in the inaccuracy of the calorimetric measurements on account of the small energies evolved.

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